height. Certain approximations are made, in that the rate of change with height of the air speed and density are neglected.

Some particular cases are worked out, but in view of the approximations made and some uncertainty as to the value of the constants in the empirical evaporation formula, and indeed as to its form, the results give an indication of the order of magnitude, rather than precise numerical estimates, when applied to natural conditions.

Finally, the effect of the wind speed, the water surface temperature, and the eddy-diffusivity, on the evaporation from a large stretch of water and the distribution of water vapour above it, is examined by varying each individually within the natural range of values. The effect of eddy-diffusivity in particular, which may vary through a large range, is found to be very pronounced.

I wish to take this opportunity of expressing my thanks to Lt.-Col. E. Gold, F.R.S., both for suggesting this problem and for his helpful criticism and advice during the course of the work.

A Study of Catalytic Actions at Solid Surfaces.[*] VI.—*Surface Area and Specific Nature of a Catalyst: two Independent Factors controlling the Resultant Activity.*

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Catalytic action is determined by two primary factors, the presence of a mechanically suitable surface at which the process takes place, and the simultaneous presence of the chemical agent (catalyst) by which the change is promoted.

The work of Langmuir,[†] Bancroft,[‡] Taylor[§] and others upon the phenomena of adsorption has emphasised anew the importance of surface with reference to catalysis. When a suitable surface is present, however, no catalytic action will occur unless on that surface (whether it be formed by an inert support or by the catalyst alone) there is a specific chemical able to form appropriate intermediate compounds with the interactants: for example, if hydrogen and ethylene are in contact with such a surface, no formation of ethane will occur unless there is present some specific material, such as palladium, platinum, nickel or copper.

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[*] Part V, 'Roy. Soc. Proc.,' A, vol. 98, pp. 27–40 (1920).

[†] 'J. Amer. Chem. Soc.,' vol. 38, p. 2221 (1916); vol. 39, p. 1848 (1917); vol. 40, p. 1361 (1918).

[‡] Presidential Address, American Electrochemical Society, 1920.

[§] 'J. Ind. Eng. Chem.,' vol. 13, p. 75 (1921).

It is probable that confusion sometimes has occurred because the respective functions of general surface and specific chemical have not been sufficiently understood to be differentiated, and an account of some work with catalytic nickel, which illustrates somewhat concisely the incidence of each factor, may therefore be of interest.

The first group of experiments correlate the apparent volume occupied by (or bulk gravity of) various catalysts with their activity; next, the rate of reduction of nickel oxide is shown to be similarly connected with bulk gravity, and finally we give an example of the relation between the degree of reduction of nickel oxide deposited upon a suitable support and the activity of the reduced catalyst in oil-hydrogenation.

Apparent Volumes of various types of Nickel Oxide and the corresponding Reduced Metals.

Kelber* showed that, whilst nickel oxide *per se*, when reduced at about 300° C., gave a moderately active catalyst, reduction of the same material at 450° C. gave a product of but feeble activity; yet nickel oxide deposited upon kieselguhr, and reduced at 450°, gave a catalyst much more active than the unsupported metal prepared at 300° C.

In the Table below are given data which compare the apparent volumes of various oxides of nickel and their reduction products with their densities, pyrophoric character and catalytic activity.

The apparent volumes were measured by shaking down the substances in narrow stoppered graduated tubes, and are given as the volume (number of cubic centimetres) occupied by 1 grm. of the material.

The samples studied were:—

(i) *Powdered fused nickel oxide*, prepared by igniting finely-divided nickel in a current of oxygen, and grinding the cooled mass of fused oxide.

(ii) *Nickel hydroxide*, prepared from the sulphate or nitrate by precipitation, washing and cautious drying.

(iii) *Nickel hydroxide on kieselguhr*, prepared as in the last case, but in presence of kieselguhr.

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* 'Ber.,' vol. 49, p. 55, 1868 (1916).

Source of reduced nickel.				Reduced nickel.			
	Density.	Apparent volume.	Temperature of reduction.	Density.	Apparent volume.	Pyrophoric character.	Catalytic activity.
		c.c.	° C.		c.c.		
Powdered fused oxide	6·96	0·35	500	8·14	0·52	None	None
Precipitated hydroxide	5·41	0·87	300 500	7·85 8·18	0·83 0·56	Pronounced Medium	Fair Very little
On kieselguhr...	1·63	3·22	500	1·85	2·67	None	Very active

Attention is drawn to the apparent volumes of the reduced precipitated hydroxide: at 300° C. this is almost the same at that of the unreduced substance, but considerable shrinkage has occurred during reduction at the higher temperature of 500° C.

The fused oxide, on the other hand, occupies less than half the bulk of the precipitated hydroxide, although its specific gravity is not much greater; and, during reduction, a certain amount of expansion (increase in porosity) is noticeable, but the product is quite inactive.

On the other hand, in the supported nickel, the kieselguhr, which does not shrink on heating, almost wholly determines the bulk of the product, and the activity is correspondingly great.

The column showing the pyrophoric character of the reduced metals is added only because it illustrates that the parallelism between this property and catalytic activity, at one time supposed to be complete, is in reality by no means so: the most active catalyst of the series is not pyrophoric, or at least only to a very small degree.

Rate of Reduction of various types of Nickel Oxide.

It has frequently been observed, with unsupported nickel oxide, that a partially reduced oxide is more active than the same when completely reduced, and this fact has been made much of by those workers who have supposed that the active agent in hydrogenation is not nickel, but a sub-oxide of the metal. Sabatier and Espil* showed, however, that, although a point of inflexion occurs in the curve showing the amount of reduction of nickel oxide (at 175° C.) against time at a point corresponding to an oxide between Ni_3O and Ni_4O, there is evidence of the presence of metallic nickel before 10 per cent. of the oxide has been reduced, and these authorities are of the opinion that the amount of nickel then present, though small, is amply sufficient to account for the hydrogenating power of the product.

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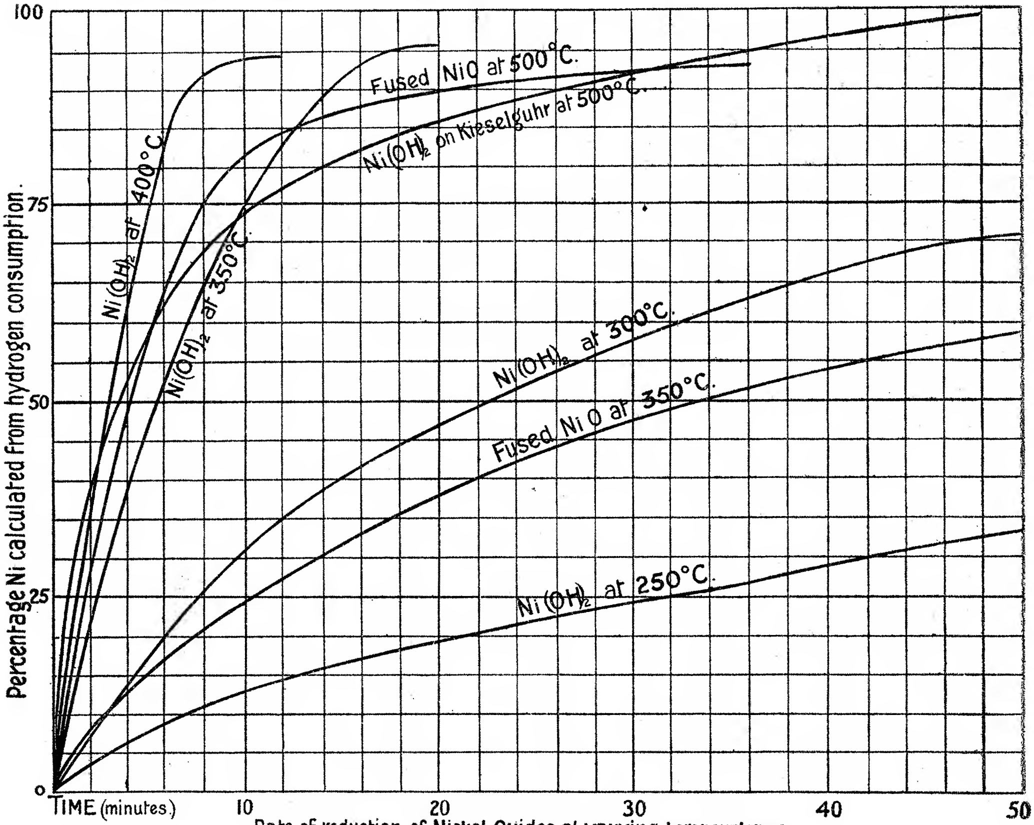
* 'Compt. rend.,' vol. 158, p. 674 (1914).

We reproduce here a series of curves (hydrogen consumed by reduction of nickel oxide/time) obtained in the reduction of the oxides quoted in the above Table, from which it appears that the point of inflexion is mainly determined by the physical state of the oxide.



Rate of reduction of Nickel Oxides at varying temperatures.

We consider that the more rapid initial reduction represents the production of metallic nickel from the surface of the oxide particles, the slower subsequent rate corresponding to the reduction of a denser central core of oxide. Since, as our bulk gravity figures show, there is a tendency to contraction when a light precipitated oxide is reduced, it is obvious that a partially reduced oxide will consist of a film of nickel dispersed over the central core of each particle, and it is practically certain that the superior activity of this product over the fully reduced metal is due to its being a "supported" catalyst (nickel distributed on nickel oxide) and therefore of the same type, although not of the same degree of activity, as nickel upon a support such as kieselguhr.

The graphs shown in the figure present the reduction of precipitated nickel hydroxide at 250°, 300°, 350° and 400° C., of the fused nickel oxide at 350° and 500° C., and of nickel hydroxide on kieselguhr at 500° C.

The curve for precipitated nickel hydroxide reduced at 250° and 300° C. shows faint points of inflexion, corresponding respectively to metallic nickel contents of about 5 and 35 per cent.; the curves for reduction at 350° and 400° C. are quite smooth up to more than 90 per cent. free nickel.

With the fused oxide, a change of curvature is noticeable at about 80 to 85 per cent. reduction at a temperature of 500° C.

Nickel hydroxide on kieselguhr reduced at 500° C. gives a smooth continuous curve, inclining more rapidly to the abscissa axis after 50 per cent. reduction has been reached; at about 60 per cent. reduction, also, the activity of the product has attained a maximum value which is thereafter constant (*vide infra*).

The reduction curves are evidently related to the physical conditions (state of the oxide and temperature of reduction) rather than to the formation of any more or less definite sub-oxides intermediate between nickelous oxide and nickel.

Relation of the Activity of a Supported Nickel Catalyst to its Reduced Metal Content.

The extent to which the solid surface most easily accessible to gases or liquids determines the extent of the activity displayed is well illustrated by overloading a support with a nickel compound and observing the activity of the products formed by gradual reduction of the latter.

Portions of a preparation of nickel oxide on kieselguhr containing a total amount of 14·62 per cent. nickel (calculated on the dry fully reduced material) were reduced in hydrogen at 350° to 500° C. to varying extents and the relative activities of the products measured roughly by the melting points of the fats produced when cotton seed oil was hydrogenated at 180° C. for one hour with an amount of the catalyst such that the total nickel present was 0·1 per cent. of the oil. The following results were obtained:—

Percentage reduced nickel.	Ratio of reduced : total nickel.	M.P. of hardened fat.
		° C.
1·89	0·129	37
3·85	0·263	50
5·57	0·381	54
7·43	0·508	59
9·16	0·631	59½
11·80	0·807	60
13·01	0·890	59½
14·21	0·972	59½

In another series of experiments the catalytic activities were compared in terms of the absorption of hydrogen per minute during the first phase of hydrogenation of the glycerides of linseed oil: we have shown* that in this stage of the hydrogenation process the graph relating hydrogen absorption to time is almost entirely linear.

Two hundred grm. of highly refined linseed oil were hydrogenated at 180° C. in presence of 2 grm. of catalyst containing a total amount of 14·50 per cent. nickel (calculated on the dry reduced catalyst), the total concentration of nickel present in the case of the fully reduced catalyst being therefore 0·145 per cent. of the weight of glyceride:—

Percentage reduced nickel.	Ratio of reduced : total nickel.	Catalytic activity.	
		H_2 absorption litres per minute.	Ratio (most active catalyst as unity).
		Measured over 11 litres.	
2·88	0·199	0·130	0·280
3·56	0·246	0·159	0·342
5·63	0·389	0·302	0·649
6·45	0·445	0·333	0·716
8·46	0·583	0·456	0·981
10·36	0·714	0·465	1·000
12·85	0·886	0·465	1·000
14·19	0·979	0·445	0·957

It is considered that figures of this nature indicate that the activity is dominated by the condition of the surface layer of reduced nickel, since it is obviously this part of the mass which will be first reduced by hydrogen to the metallic state.

It is notable that, as in the case of "non-supported" nickel catalysts, maximum activity is reached when only a portion of the nickel oxide has been reduced to the metallic state, but in the present case the support itself is not appreciably affected in bulk by the process of reduction, and, instead of declining again, the catalytic activity is maintained constant until and when the whole of the nickel oxide present has been reduced.

Comparison of the activity of the supported and non-supported catalysts, in the light of the parallel observations on the bulk gravities of the materials, leads inevitably to the conclusion that these variations in catalytic power are to be ascribed simply to the different surface areas of free nickel exposed, and do not require for their interpretation the assumption of the presence of any catalyst other than metallic nickel.

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* 'Roy. Soc. Proc.,' A, vol. 96, pp. 137–146 (1919).